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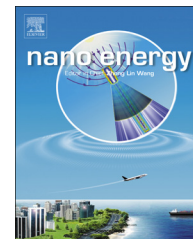
RAPID COMMUNICATION

Highly stable rGO-wrapped Ni_3S_2 nanobowls: Structure fabrication and superior long-life electrochemical performance in LIBs

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Abstract

Uniform Ni_3S_2 nanobowls with an average size of 250 nm and shell thickness of $\sim$30 nm wrapped by rGO sheets were firstly synthesized by a simple wet chemical method. The Ni_3S_2-rGO hybrid composite with spatial three-dimensional (3D) structure showed enhanced electrochemical properties in lithium-ion batteries, compared with Ni_3S_2 hollow chains. Its specific capacity could be up to 443 mA h g^{-1} at 0.5 C after 500 cycles (theoretical capacity of Ni_3S_2 is 462 mA h g^{-1}), while Ni_3S_2 hollow chains faded dramatically to 147 mA h g^{-1} after 100 cycles. The improved cycle stability of the composite could be ascribed to the bowl structure with both exposed interior and exterior arch surfaces which could stand much more lithiation-delithiation than quasi-1D hollow chains. The novel stable bowl-like structure, the wrapped flexible rGO sheets served as buffers for the expansion of Ni_3S_2 bowls, the attachment sites provided by bowls keeping rGO from aggregation, and the improved electron transfer rate by rGO sheets, all synergetic effects made the composite a superior anode material. Furthermore, an efficient simple method was proposed to check componental transform during cycles by comparing the peak ratio in S2p spectrum when sulfides were used as electrode materials in LIBs.
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Introduction

Although lithium ion batteries (LIBs) have been widely used in many kinds of electric devices, low specific capacity and poor cycle stability restrict their further development. Some transition metal oxides or sulfides have been studied instead of

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traditional graphite anodes as their high lithium activity and considerable theoretical capacity [1]. However, these anode materials suffer from irreversible expanded volume and easily pulverized structures during lithium ions insertion/extraction processes [2]. The in-situ TEM techniques gave direct evidences, for example, Gregorczyk et al. reported in situ cycling of RuO$_2$ anode with a volume expansion of 95% after lithiation and 26% irreversible after delithiation [3], while Kushima et al. observed the leapfrog cracking in ZnO nanowires during electrochemical lithiation [4]. Therefore, it is significant to design stable nanostructures and to seek efficient structure buffer for developing high-performance LIBs.

What kind of nanostructure is suitable for electrode materials in LIBs? Compared with hollow spheres or other closed hollow structures, the peculiar bowl-like nanostructure with open interior and exterior arc surfaces could not only provide bigger specific surface area but also alleviate structure collapse by counteracting part of the force caused by Li$^+$ insertion and extraction, leading to high structure stability in the charge/discharge process. The bowl-like structure has rarely been used as anode materials in LIBs. Besides, graphene or reduced graphene oxide (rGO) sheets are excellent substrates to protect electrodes from pulverization and to enhance the electrochemical performances as their large specific surface area, high conductivity and good mechanical flexibility [5].

In this paper, a wet chemical method was used to synthesize the Ni$_3$S$_2$ nanobowls–rGO (NBs–rGO) composite for anode materials of LIBs for the first time. The rGO sheets serve as buffer for the volume expansion of Ni$_3$S$_2$ NBs during charge/discharge processes, while nanobowls serve as attachment sites for rGO sheets and prevent them from aggregation [6]. To confirm the synergetic effect of Ni$_3$S$_2$ NBs and two-dimension (2D) rGO sheets on lithium storage capacity, conductivity and cycling performance, Ni$_3$S$_2$ hollow chains and rGO sheets were separately used as electrode materials for comparison. The relationship between persistence of nanostructure and long-term cycle stability was disclosed, giving suggestion on designing optimal structures for electrode materials with superior electrochemical performance.

Experimental section

Chemical reagents and materials

Graphite powder (325 mesh with purity > 99.99%), polyvinyl pyrrolidone (PVP, average M_W = 58,000), Polyvinylidene fluoride (PVDF), acetylene black (AB) and N-methyl-2-pyrrolidone (NMP) were obtained from Alfa Aesar. Polypropylene separator (Celgard 2400) purchased from Celgard. Electrolyte of LiPF$_6$ (1 mol L^{-1}) in ethylene carbonate (EC) and diethyl carbonate (DMC) (1:1, v/v) was purchased from Tianjin Jinniu Power Sources Material Co., Ltd., China. All other chemicals (purchased from Beijing Chemical Co., Ltd., China) were analytical grade and used without further purification. Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummer's method as originally proposed by Kovtyukhova et al. [7]. GO was dialysed for 7 days to remove metal ions and acids. The brown suspension of GO sheets was treated by centrifugation at 10,000 rpm for 5 min to remove any undispersed solid. The GO powder obtained by freeze drying was used to prepare aqua-suspension with a concentration of 4.5 mg mL^{-1}.

Preparation of the Ni$_3$S$_2$ NBs–rGO composite

In a typical synthesis of the Ni$_3$S$_2$ nanobowls-reduced graphene oxide composite (the Ni$_3$S$_2$ NBs–rGO composite), 3 mL of GO solution (4.5 mg mL^{-1}), 0.119 g of NiCl$_2 \cdot$6H$_2$O and 0.133 g of PVP were dispersed in 50 mL of ethylene glycol (EG) by sonication for 2 h. Then, 0.2 mL of hydrazine monohydrate liquid (80%, v/v) was added into the mixture. Afterwards, the solution was heated in an oil bath under magnetic stirring at 168 °C. It turned black in a few minutes and then kept at 168 °C for one hour and a half. Subsequently, the black solution was dropwise added the mixture of thiourea (2 mmol) and EG (20 mL), and maintained for 2 h under magnetic stirring. The as-synthesized product was washed with deionized water and ethanol several times and dried by freeze drying.

Preparation of Ni$_3$S$_2$ hollow nanochains

The Ni$_3$S$_2$ hollow nanochains were synthesized as described above without GO solution, according to the method we reported before [8].

Preparation of rGO

The way of prepared rGO was similar with Ni$_3$S$_2$ NBs–rGO composite but no NiCl$_2 \cdot$6H$_2$O was added.

Characterizations

The structure and the composition of the as-prepared samples were characterized by X-ray powder diffraction (XRD, Rigaku Dmax 2200) with Cu Kα radiation (λ=1.5416 Å). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) investigations were carried out using a JEOL JEM-2100F microscope. Raman spectrometer was recorded on a Lab RAM HR800 (HORIBA Jobin Yvon) confocal Raman spectrometer, with an excitation laser wavelength of 514.5 nm. The electrochemical performances of the Ni$_3$S$_2$ NBs–rGO composite, Ni$_3$S$_2$ nanochains and rGO were used as anode materials and separately investigated in a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics Co. Ltd., China) with a voltage range of 0.05–3 V. The cyclic voltammetry (CV) was performed on CHI660D electrochemical workstation (Shanghai Chenhua Co. Ltd., China) with a potential range of 0.005–3 V vs. Li/Li$^+$ at a scan rate of 0.5 mV s^{-1}. The Electrochemical impedance spectroscopy (EIS) measurements were carried out using the electrochemical workstation with a frequency chosen from 100 kHz to 0.1 Hz. Thermogravimetric analysis (TGA) was performed in air using a Pyris Diamond TG/DTA (PerkinElemer Inc., U.S.A). X-ray photoelectron spectroscopy (XPS) data were obtained using an ESCALab250 electron spectrometer from Thermo Scientific Corporation with monochromatic 150 W Al Kα radiation under a pressure of about 6.5×10^{-10} mbar.